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Supporting Information

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Mechanism of Glucose Isomerization Using a Solid Lewis Acid Catalyst in Water**

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Supplementary Material

1.- Experimental

1.1.- Zeolite synthesis (Sn-Beta and SnO_2-Beta)

Zeolites were prepared as follows: 7.57 g of tetraethylammonium hydroxide solution (Sigma-Aldrich, 35% (w/w) in water) was diluted with 15 g of water. Next, 7.011 g of tetraethylorthosilicate (Sigma-Aldrich, 98% (w/w)) was added, followed by the addition of 0.121 g of tin (IV) chloride pentahydrate (Sigma-Aldrich, 98% (w/w)) or 0.052 g of tin dioxide (Sigma-Aldrich), depending if Sn-Beta or SnO_2-Beta were synthesized. The mixture was stirred until complete hydrolysis of the tetraethylorthosilicate was achieved, and then allowed to reach the desired water ratio by complete evaporation of ethanol and some water. Finally, 0.690 g of HF solution (Mallinckrodt, 52% (w/w) in water) was added, resulting in a thick gel. The gel composition was SiO_2 / 0.01 $SnCl_4$ / 0.55 TEAOH / 0.54 HF / 7.52 H_2O. The gels were transferred to Teflon-lined stainless steel autoclaves and heated at 413 K for 25 days. The solids were recovered by filtration, washed extensively with water, and dried at 373 K overnight. The solids were calcined at 853 K for 6 h to remove the organic content located in the crystalline material. X-ray diffraction confirmed that the solid materials have the Beta zeolite topology (not shown), and SEM EDS measurements for the Sn-Beta sample show an atomic ratio Si:Sn of 96:1, and an atomic ratio of Si:Sn of 112:1 for SnO_2-Beta .

1.2.- Characterization

Powder X-ray diffraction (XRD) patterns were collected using a Scintag XDS 2000 diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) measurements were recorded on a LEO 1550 VP FE SEM at an electron high tension (EHT) of 10 kV. UV-Vis measurements were recorded using a Cary 3G spectrophotometer equipped with a diffuse reflectance cell. ^{1}H and ^{13}C NMR spectra were recorded using a Varian INOVA 500 MHz. Proton and carbon chemical shifts are reported to the residual solvent signal.

1.3.- Catalytic tests

Isomerization experiments were carried out in 10 ml thick-walled glass reactors (VWR) heated in a temperature-controlled oil bath placed on top of a digital stirring hotplate (Fisher Scientific). In a typical experiment, 1.5 g of an aqueous solution composed of 10% (w/w) glucose and the corresponding catalyst amount to achieve a 1:50 metal:glucose molar ratio were added to the reactor and sealed. The reactor was placed in the oil bath and removed at specific times. The reaction was stopped by cooling the reactor in an ice bath, and small aliquots were taken for analysis. Sample analyses were performed by means of high performance liquid chromatography (HPLC) using an Agilent 1200 system (Agilent Technologies Corp.) equipped with PDA UV (320 nm) and evaporative light-scattering (ELS) detectors. Glucose, fructose, and mannose concentrations were monitored with a Biorad Aminex HPX87C (300 x 7.8) column (Phenomenex), using ultrapure water (pH = 7) as the mobile phase at a flow rate of 0.60 ml/min and a column temperature of 353 K.

2.- Figures

Figure S1: Meerwein-Ponndorf-Verley (MPV) reaction pathway. R = alkyl or aryl; R_1 and R_3 = alkyl or hydrogen; Me = metal

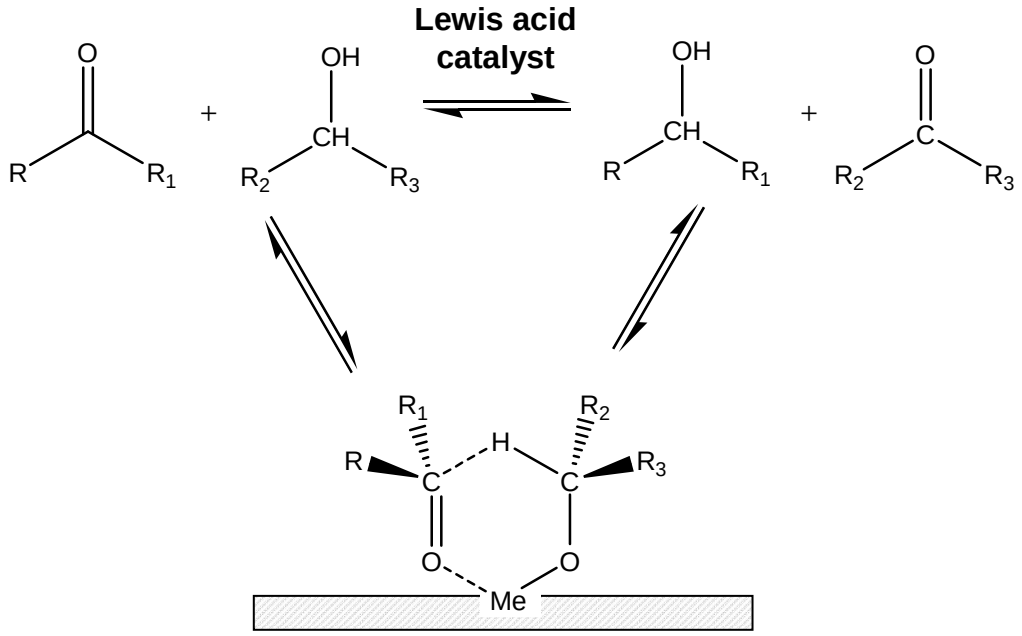
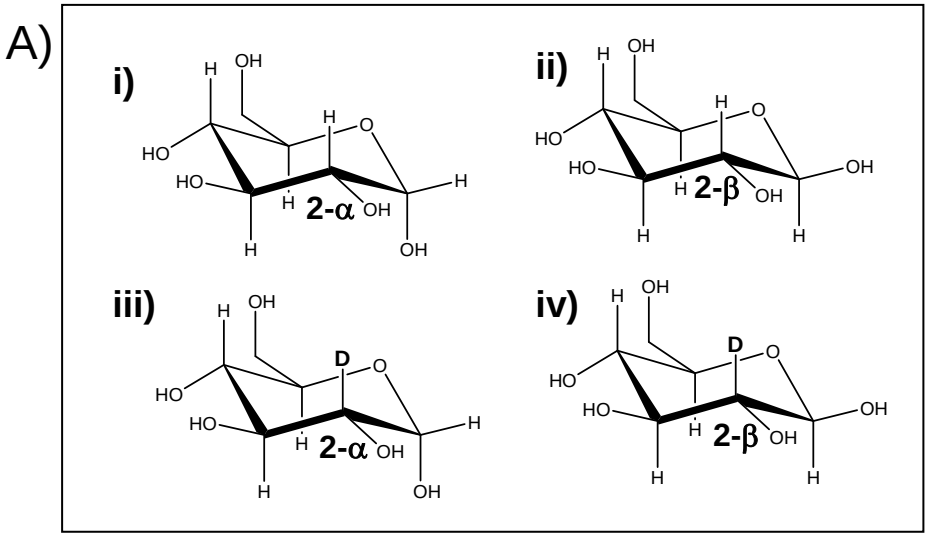
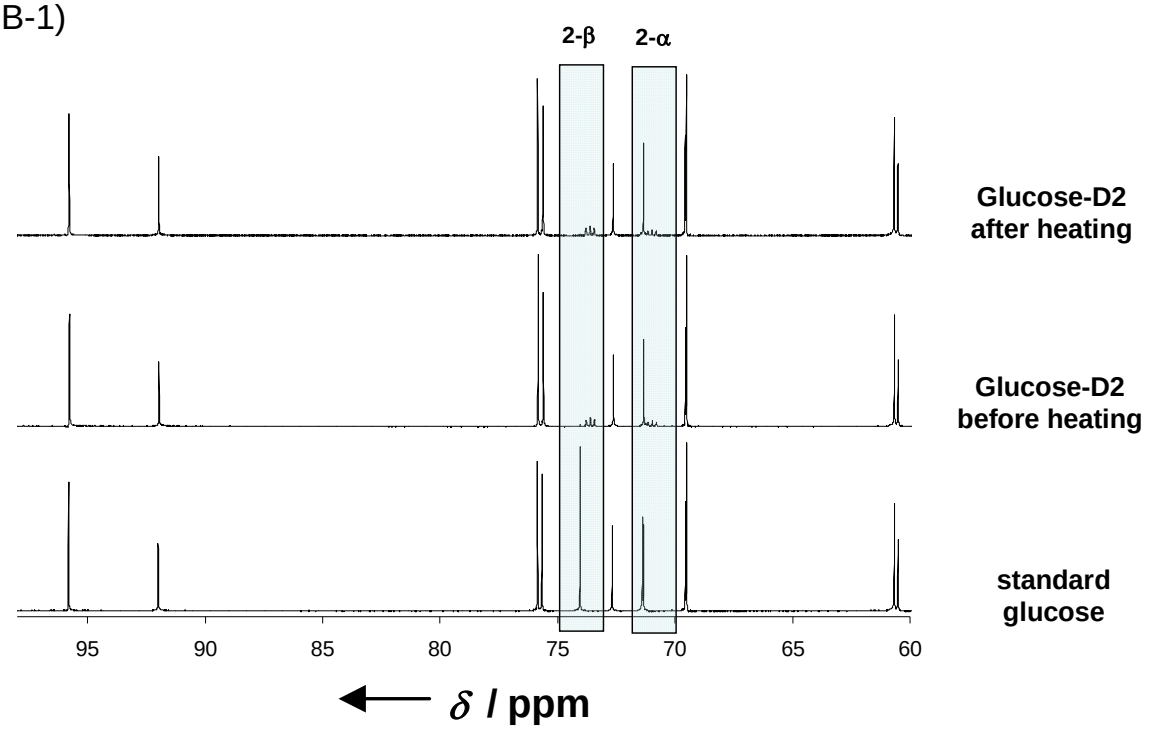


Figure S2: A) An unlabeled glucose solution contains 35% glucose in the α-pyranose configuration (i) and 65% in the β-pyranose configuration (ii). The same ratios are obtained for labeled glucose (glucose-D2), where 35% is in the α-pyranose configuration (iii) and 65% is in the β-pyranose configuration (iv).

B) ^{13}C NMR spectra of unlabeled glucose, glucose-D2 before heating, and glucose-D2 after heating at 383 K without a catalyst.



B-1)


2-β
2-α
Glucose-D2
after heating
Glucose-D2
before heating
standard
glucose
95
90
85
80
75
70
65
60
δ / ppm

B-2)

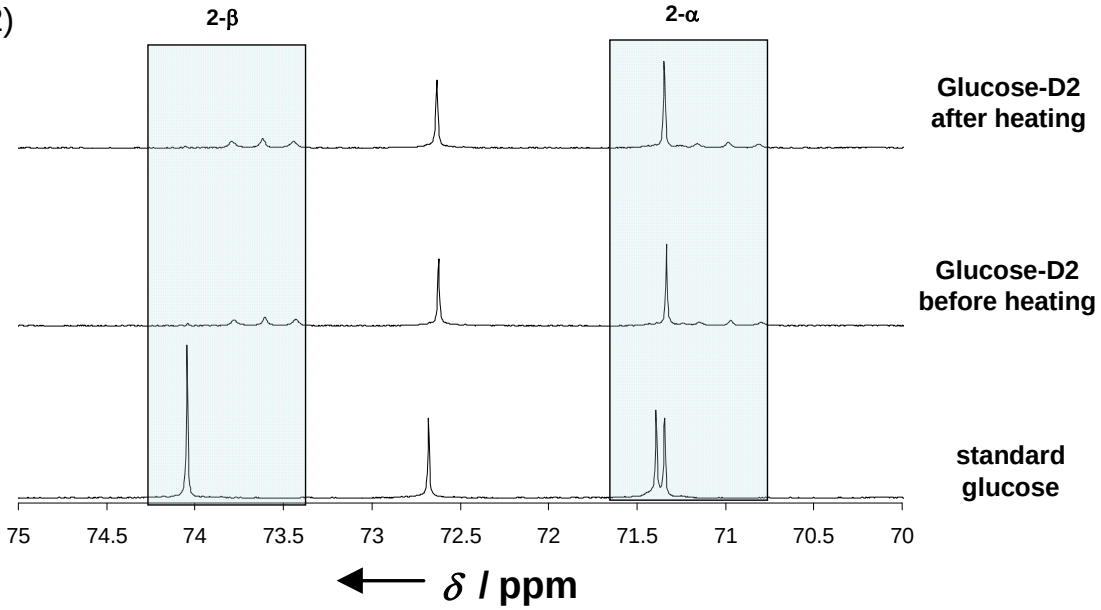

2-β
2-α
Glucose-D2
after heating
Glucose-D2
before heating
standard
glucose
75
74.5
74
73.5
73
72.5
72
71.5
71
70.5
70
δ / ppm

Figure S3: Glucose isomerization conversion profile at 383 K, using Sn-Beta as catalyst. Reaction conditions: 10 wt% glucose (unlabeled or labeled) in water and 1:50 Sn:glucose molar ratio.

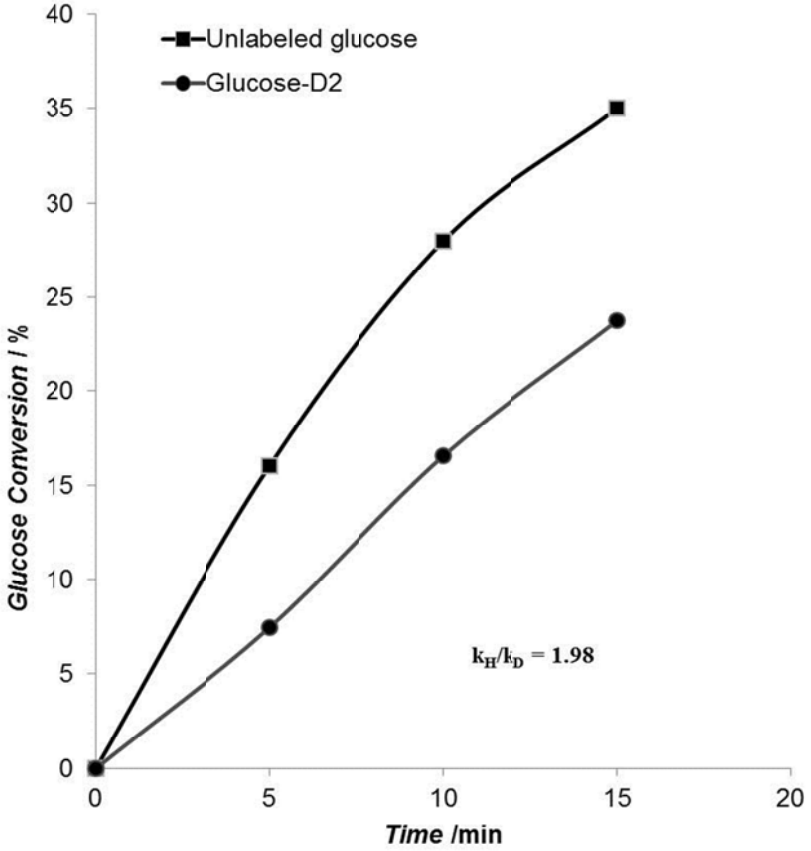


Figure S4: A) Glucose isomerization reaction and product distributions (glucose-gray, fructose-white, and mannose-black) after 45 minutes at 383 K using Sn-Beta or SnO_2-Beta. Reactions were performed with a 10 wt% glucose solution, using the corresponding amount of catalyst to maintain a 1:100 metal:glucose molar ratio. B) Diffuse reflectance UV-Vis spectra for Sn-Beta and SnO_2-Beta.